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SPACE PROCESSING OF ELECTRONIC MATERIALS

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SPACE PROCESSING OF ELECTRONIC MATERIALS

1. Introduction

The major thrust of the electronic materials program at the Space Science Laboratory in the past year has been toward the bulk growth of solid solution alloys of mercury telluride and cadmium telluride. These alloys are usually described by the formula $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, and are useful for the construction of infrared detectors. The electronic energy band gap can be controlled between zero and 1.6 electron volts by adjusting the composition x . The most useful materials are at $x \sim 20\%$, suitable for detecting wavelengths of about 10μ meters. The problems of growing large crystals are rooted in the wide phase diagram of the HgTe-CdTe pseudobinary system which leads to exaggerated segregation in freezing, constitutional supercooling, and other difficulties, and in the high vapor pressure of mercury at the growth temperatures, which leads to loss of stoichiometry and to the necessity of working in strong, pressure resistant sealed containers. Several excellent reviews of the state-of-the-art at the beginning of the contract period are available, and so none is offered here. (See, for example, Willardson and Beer, editor: "Mercury Cadmium Telluride", Semiconductors and Semimetals, Vol. 18, Academic Press, New York 1981).

Among the puzzles associated with Bridgman growth of HgCdTe are two toward the solution of which substantial progress has been made during the contract period. The first is the failure of thermal models to predict, even qualitatively, the shape of the liquid-solid interface during crystal growth. Second is the occasional unexplained

rupture at low temperature of ampoules which have satisfactorily withstood much higher temperatures and pressures. These ruptures have been called "benign", because the charge is generally solid and the rupture energy is low, but nevertheless they definitely terminate any further work with the ampoule. The two principal research areas, thermal conductivity and molar volume studies, have cast significant light on these mysteries.

2. Thermal Conductivity

The thermal conductivity of HgCdTe solid and melts may well be strongly dependent on temperature, varying as much as an order of magnitude. If this is the case, and if the melt conductivity is higher than that of the crystal, then the behavior of the melt growth face shape would be in part explained.

Since HgCdTe melts must be contained in strong sealed silica ampoules, it is difficult to make local temperature measurements in them, and so direct measurements of thermal conductivity are difficult. Fortunately an alternative exists: the thermal diffusivity can be measured without precise measurement of temperature, and this can be used to calculate the thermal conductivity. The diffusivity is given by

$$\alpha = \frac{k}{\rho C_p}$$

in which ρ is the density, already known with high precision, C_p is the specific heat which can be reasonably accurately estimated on

theoretical grounds, and k is the thermal conductivity. The dimensions of diffusivity are

$$[\alpha] = \frac{[\text{length}]^2}{[\text{time}]}$$

and so in principle the measurement of α can be reduced to a "scale and stopwatch" effort in which the container does not interfere.

Thermal diffusivity measurements can be reduced to two classes: the Angstrom method and the pulse method. In the Angstrom method a long thin rod is heated periodically at one end, and the resulting heat waves are monitored as they travel along the rod. The phase shift over a measured length between two sensors is determined, and from this the time and length are obtained to compute α . In the pulse heating measurements a thin flat plate is heated by a flash lamp or laser pulse on one side, and the resultant temperature rise on the opposite face is timed. The thickness of the sample is the length used in calculating α . Both of these methods are under study, and indications are that either can give good results. The Angstrom method theory has been worked out for the case of HgCdTe melts in long fused silica tubes with thick walls, but no hardware has as yet been built. Since the flash heating system seemed closer to fruition, hardware development effort was concentrated in this area.

A method for making strong, thick walled fused silica cells with flat windows was developed under a previous contract and is described in the Final Report for NASA Contract NAS 8-32920. During the present contract period an improvement has been made in the management of the

window polishing system so that the production of finished windows is greatly increased. The windows are now polished in sets of three, and as soon as only two are sufficiently flat and smooth they are "harvested". The third is saved and subsequently finished with two others similarly saved. In this way protracted overpolishing of the first windows is avoided, which saves time and also greatly reduces the risk of inadvertent scratching.

A serious problem was encountered with cracks which appeared in the cells after loading. It was clear early in the program that the cells were sufficiently strong to withstand the vapor pressure of mercury encountered during the high temperature phase of reacting and homogenizing the charge. Nevertheless, when nearly but not quite all of the cells were examined after cooling, cracks were observed in the plane of and extending outward from the edges of the cell cavity. This cracking reduced the total yield of cells to less than 10% of those loaded. Figure 1 shows a cell with a typical crack.

During the molar volume project, to be described below, it was found that the volume of solid HgCdTe is greater than that of the melt. Furthermore it was observed that when solutions of CdTe in HgTe begin to freeze, the CdTe rich solids which first form float very quickly to the top. In this way a slow freeze, or several quick freeze cycles enrich the top of the charge in CdTe . This in turn results in a higher liquidus temperature at the top of the charge, so that in a uniform field of decreasing temperature, freezing starts from the top down. When this happens in a thermal diffusivity cell, the neck between the cell cavity and the stem is plugged with solid while the cavity is

is still filled with liquid. As this liquid freezes it must expand, and as the escape to the stem is not blocked, the faces of the cell cavity are pushed apart with great force but limited possible displacement. In this way cracks are started which propagate for a short distance but stop before reaching the outside of the cell.

Once this was understood it became clear that a rapid freeze, from the bottom of the cell upward into the stem is essential. During cooling the cell must stay between the liquidus and solidus temperatures for as short a time as possible so as to limit segregation of CdTe, and material in the neck of the cell must remain liquid until that in the cell cavity is completely frozen. A method has been worked out (see Figure 2) which provides a directional quench after homogenization in the rocking furnace. The cell is completely wrapped in ceramic fiber insulation except for a small surface at the very bottom. It is then placed in the rocking furnace and heated with the stem down, so that the charge does not enter the cell until reaction and homogenization are complete. Homogenization is accomplished by rocking in which the rocking furnace is limited at the horizontal by a stop so that melt cannot pass into the cell. After an hour of this process the furnace is rotated to the vertical with the cell stem up and the cell is charged. The cell is then lowered to the end of the rocking furnace tube to expose its uncovered bottom surface, and is chilled by a jet of cold air.

In this way a series of eight cells was loaded at the end of the contract period with a 100% yield.

Cells with the following characteristics have been sent to the Thermophysical Properties Research Laboratory at Purdue University for measurement:

#	X	Solidus (°C)	Liquidus (°C)	Thickness (mm)
1	0.205	707	794	1.371
2	0	670	670	1.797
3	0.051	679	702	1.341
4	0.107	689	731	1.412
5	0.301	727	841	1.485
6	0.204	707	794	1.438
7	0	670	670	1.161
8	0.053	679	703	1.221

Preliminary indications are that good measurements of thermal diffusivity can be made with these cells. The thermal conductivity of the melt appears to rise rapidly with temperature in a way that may explain completely the failure of our older thermal models.

3. Molar Volume

During the contract period a large effort has gone into the measurement of the molar volume of HgCdTe alloys as a function of temperature. This work is an outgrowth of Dr. Holland's 1980 observation that the density of HgTe melts is higher than that of the solid, and that in fact the maximum density is at a temperature $\sim 50^{\circ}\text{C}$ above the melting point. The effect is associated with the change in chemical bond from the covalent bond characteristic of the zincblende type solid semiconductor to the more metallic nature of the melt. Since HgTe dissociates to a considerable extent in the melt, the melt has in fact many characteristics which would be expected of dilute metallic mercury, such as the high thermal diffusivity mentioned in the previous section of this report.

The experimental procedure is based on ampoules with a 10 mm I.D. body about 10 cm long and a 5 mm I.D. stem of about the same length. These ampoules are loaded with HgCdTe of various compositions and in such an amount that when they are heated in a vertical, stem up position, the melt meniscus is somewhere about midway up the stem. The stems have witness marks made by welding around them a fused silica fiber, and thus the ampoule might be thought of as a thermometer with a very large capillary bore and only one mark on the temperature scale. The ampoules are heated in a furnace which has a semitransparent gold film on glass mirror to contain the infrared radiation while at the same time permitting visual observation of the interior. A cathetometer with a 2 x telescope is positioned so as to

measure the meniscus height relative to the witness mark. A change in meniscus height multiplied by the stem bore area gives a change in volume, and so the thermal volume expansion of the liquid can be calculated.

Figure 2 is a graph of a typical data run. Note that during heating the meniscus is high and moves up and down irregularly. This is because during heating the mercury vapor pressure in the vapor space above the melt increases rapidly, and the necessary mercury must come out of the melt. Since the process is too rapid for diffusion to supply, bubbles of mercury vapor form in the melt, raising the meniscus level. When these bubbles rise to the top of the melt and break, the meniscus then drops again. During cooling the complementary process is a "rain" of mercury, which does not significantly affect the meniscus, and so a smooth curve results, from which reliable thermal expansion figures may be calculated. Note also that freezing is not complete at the solidus temperature. The last to freeze is Cd depleted.

It has been very revealing to watch the actual freezing process as it happens in the ampoule. If HgCdTe alloys are held between the solidus and liquidus temperatures, then CdTe rich solids form. These are quite bouyant, not only because Cd is lighter than Hg, but also because the solid molar volume is larger. That these solids float to the top is readily visible in the transparent furnace, as the meniscus roughens with solid particles projecting through it. If freezing then continues, a solid plug forms at the top of the melt.

Further cooling results in expansion of the material below the plug. If the plug cannot slide upward, then usually a ribbon of solid is extruded through a hole in the center of the plug, often followed by the "benign" rupture of the ampoule body. In these ruptures the ampoule splits down the side and there is some mercury lost as vapor, but most of the solid is retained. The ampoule material stays with it and does not shatter.

4. Other Work in the Laboratory

During the contract period the rocking furnace was completely rebuilt using a new furnace muffle made by Ohio Thermal Corp. to our design. Fixtures were added to lock the furnace in a variety of positions for loading and casting, and steps were made so that the furnace swing could be limited at the horizontal position for homogenizing the thermal diffusivity cell charges.

The new ampoule loading distillation apparatus is nearing completion. The vacuum system is complete and leak tight, the heater installed and operational, and the mechanical scanning system operating. The only remaining item to be installed is the shutter which separates the ampoule from the evaporator during the preliminary outgassing process.

Dr. Holland attended the Gordon Conference on crystal growth at Plymouth, NH, in July 1982.

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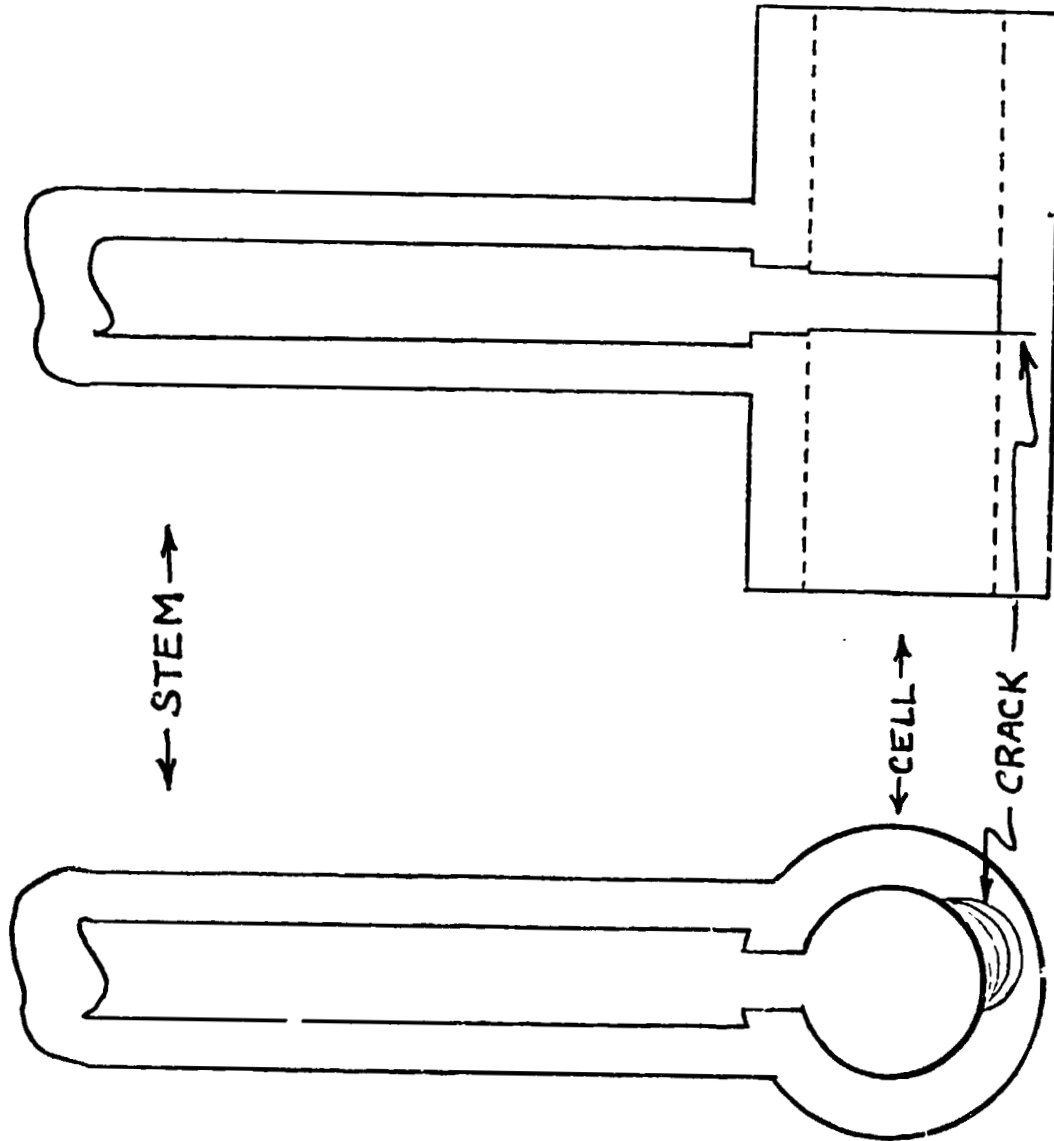


FIGURE 1

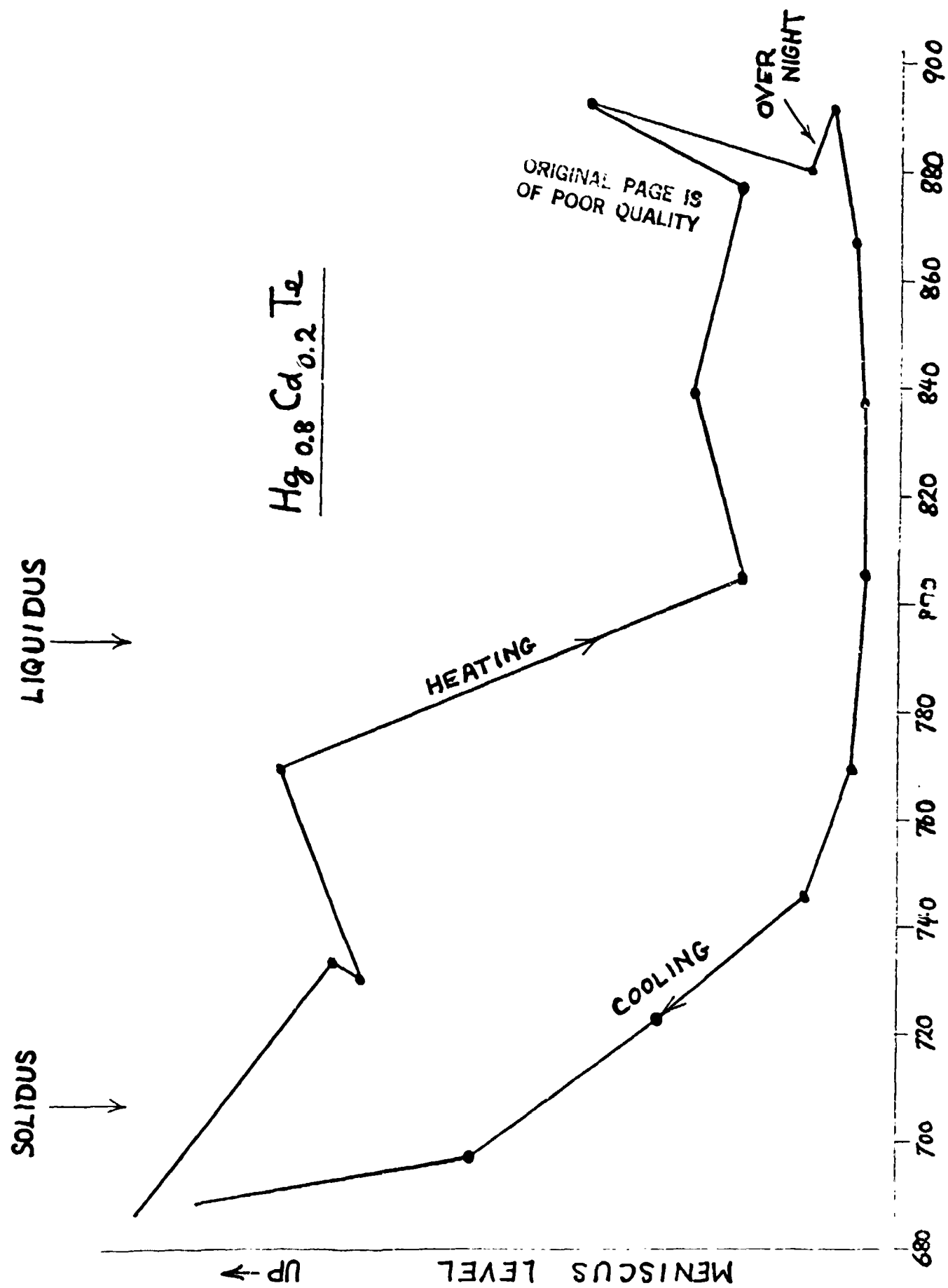


FIGURE 2